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Identification and optimization of advanced phosphors using combinatorial libraries

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A combination of thin-film deposition and physical masking steps were used to generate libraries of the rare earth activated refractory metal oxides, $\text{Gd}(\text{La},\text{Sr})\text{AlO}_x$. Systematic variation of composition and processing conditions afforded tricolor phosphors with the following nominal compositions, $(\text{Gd}_{0.46}\text{Sr}_{0.31})\text{Al}_{1.23}\text{O}_x\text{F}_{1.38}:\text{Eu}^{2+}_{0.06}$ (green), $\text{La}_{0.5}\text{Al}_{1.5}\text{O}_x:\text{Eu}^{2+}_{0.04}$ (blue), and $\text{Gd}_{0.77}\text{Al}_{1.23}\text{O}_x:\text{Eu}^{3+}_{0.06}$ (red), which had quantum efficiencies of $\geq 94\%$, $\approx 60\%$, and $\geq 93\%$, respectively at $\lambda_{\text{max}}^{\text{ex}}$. The high quenching temperatures ($250\text{--}350\text{ }^\circ\text{C}$), good chromaticities and refractory nature of these phosphors are desirable features for display applications. © 1997 American Institute of Physics. [S0003-6951(97)01823-8]

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There is considerable interest in the development of phosphors for applications in advanced display technologies including plasma, field emission, electroluminescent, and CRT projection displays. Although the photophysical processes leading to luminescence are relatively well understood, the specific spectral properties, luminescence efficiencies, and operational lifetimes depend on complex interactions between the excitation source, host lattice, sensitizer, and luminescent center. Consequently, the identification of phosphors that are ideally suited to the requirements of a given display technology is highly empirical and likely to benefit from a combinatorial approach. Here we illustrate the effectiveness of such methods by the rapid identification and optimization of tricolor phosphors of rare earth activated refractory metal oxides, $\text{Gd}(\text{La},\text{Sr})\text{AlO}_x$.

Oxides are attractive host materials for the development of advanced phosphors due to their ease of synthesis and stability. For example, the efficient refractive oxide phosphors, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (red),¹ $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Tb}^{3+}$ (green),² and $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (blue),³ have found applications in tricolor lamps, projection TVs, and plasma displays as a consequence of their high "thermal quenching" temperatures, and resistance to deterioration under the harsh conditions of intense plasma, vacuum UV, or electron beam excitation. The combinatorial libraries were used to rapidly survey a wide range of compositions of oxides under a variety of processing conditions. Phosphors with properties of interest were reproduced by conventional bulk solid state synthesis and powder samples were analyzed in detail to obtain photophysical and structural information.

Libraries of thin film phosphors derived from aluminate hosts were generated by using a combination of rf sputtering and physical masking steps to generate different elemental compositions (Fig. 1).^{4,5} The sputtering targets ($>99.9\%$ purity) included La_2O_3 , Y_2O_3 , GdF_3 , SrCO_3 , Al_2O_3 , EuF_3 , Tb_2O_7 , and CeO_2 ; libraries were deposited on polished (100) LaAlO_3 , MgO , or Si single crystal substrates. The amount of precursors deposited was monitored *in situ* with a quartz crystal thickness monitor (calibrated by an electronic microbalance). Subsequent analysis with a profilometer re-

vealed that film thickness varied less than 5% over a 2 in. diameter deposition area. Up to seven identical libraries can be fabricated at once. These identical libraries were annealed under different partial pressures of O_2 , H_2 , He , and Ar and temperatures ranging from $1100\text{ }^\circ\text{C}$ to $1400\text{ }^\circ\text{C}$ for up to 4 h. The refractory nature of the precursors used in these materials prevents significant changes in stoichiometry due to thermal evaporation. Indeed identical samples in a library afforded the same relative luminescent intensities and chromaticities. Photoluminescence images were obtained by color photography under broad wavelength UV irradiation (Hg lamp) (Fig. 1). Due to limitations of space, detailed maps indicating the stoichiometry of each sample in each library will be described elsewhere.⁶

As is evident from Fig. 1, the thin film combinatorial approach is very effective in the qualitative evaluation and correlation of the luminescent properties of phosphors. Compounds with the following nominal compositions, $\text{Gd}_{0.77}\text{Al}_{1.23}\text{O}_x:\text{Eu}^{3+}_{0.06}$, $\text{Gd}_{0.46}\text{Sr}_{0.31}\text{Al}_{1.23}\text{O}_x\text{F}_{1.38}:\text{Eu}^{2+}_{0.06}$ and $\text{La}_{0.5}\text{Al}_{1.5}\text{O}_x:\text{Eu}^{2+}_{0.04}$, afforded the brightest red, green, and blue photoluminescence, respectively. Red phosphors with the composition $\text{LaAlO}_x:\text{Eu}^{3+}_y$ ($y < 0.01$)⁷ and $\text{GdAlO}_x:\text{Eu}^{3+}_y$ ($y < 0.01$)⁸ have previously been reported, but not optimized or characterized with regard to their quantum efficiencies. To fully characterize these tricolor phosphors, bulk samples corresponding to the stoichiometry of the brightest phosphor of each compositional series in the libraries were synthesized by standard solid state synthetic methods.

Quantum efficiencies (QE) of 90% were obtained for both the red phosphor $\text{Gd}_{0.77}\text{Al}_{1.23}\text{O}_x:\text{Eu}^{3+}_{0.06}$ and the green phosphor with composition $(\text{Gd}_{0.46}\text{Sr}_{0.31})\text{Al}_{1.23}\text{O}_x\text{F}_{1.38}:\text{Eu}^{2+}_{0.06}$ relative to the commercial phosphors $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (red, QE = 97%)⁹ and $\text{LaPO}_4:\text{Tb}^{3+}, \text{Ce}^{3+}$ (green, QE = 93%),⁹ respectively. In each case quantum efficiency was determined by exciting at $\lambda_{\text{max}}^{\text{ex}}$, using a standard comparative method.¹⁰ It was found that $\lambda_{\text{max}}^{\text{ex}}$ of $\text{Gd}(\text{La})_m\text{Sr}_n\text{AlO}_x:\text{Eu}^{2+}_y$ is red shifted relative to the commercial oxide phosphors, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{LaPO}_4:\text{Tb}^{3+}, \text{Ce}^{3+}$, the $\lambda_{\text{max}}^{\text{ex}}$ of the red phosphors $\text{Gd}_m\text{AlO}_x:\text{Eu}^{3+}_y$ is $\sim 275\text{ nm}$ and the $\lambda_{\text{max}}^{\text{ex}}$ of the green phosphor $\text{Gd}(\text{La})_m\text{Sr}_n\text{AlO}_x:\text{Eu}^{2+}_y$ is $\sim 300\text{ nm}$. In general, the bulk samples qualitatively reproduced the luminescent properties of the samples contained in the libraries, i.e.,

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TABLE I. Proj

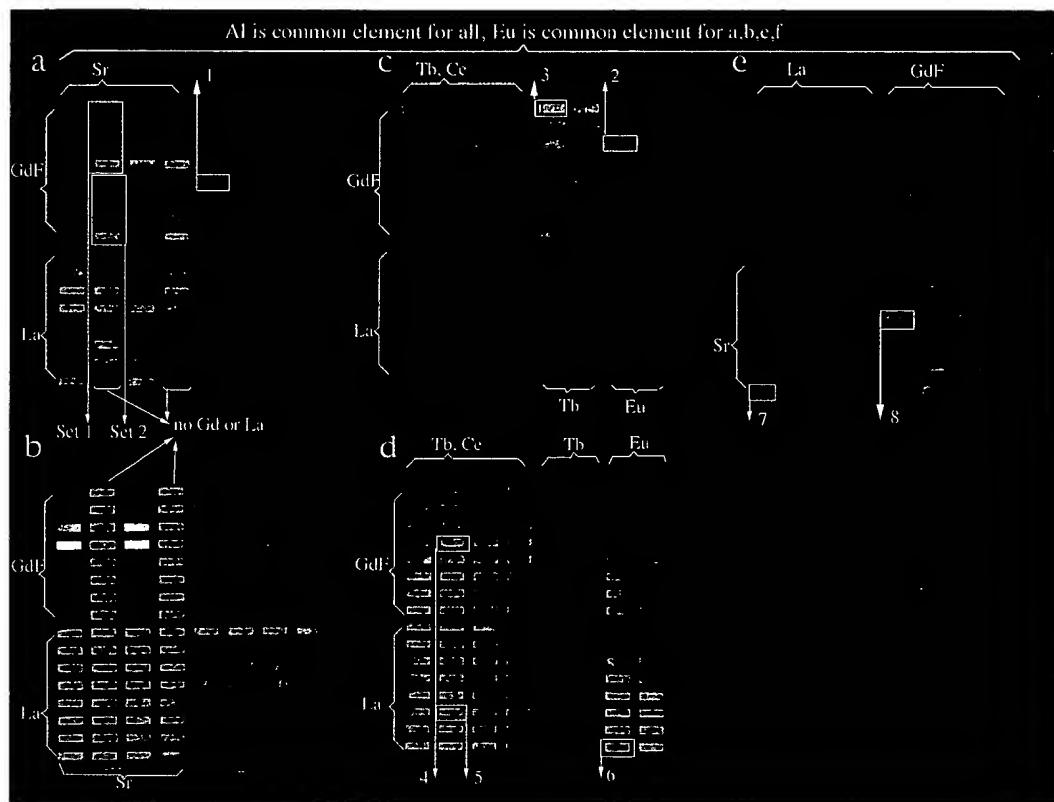


FIG. 1. Photoluminescent images of a series of phosphor libraries with the indicated nominal compositions processed under different conditions: (a) La (or $\text{GdF}_3\text{Sr}_n\text{AlO}_x\text{Eu}_y^{2+3+}$ where $0.375 \leq m \leq 1$, $0.25 \leq n \leq 0.4$, $1.88 \leq y \leq 12\%$ in atomic ratio), were annealed at 1150°C in $10\% \text{H}_2/\text{Ar}$ for 4 h; (b) same as (a), but annealed at 1400°C in $40\% \text{H}_2/\text{He}$ for 4 h; (c) La (or $\text{GdF}_3\text{Sr}_n\text{AlO}_x\text{Eu}_y^{2+3+}(\text{Ce}_z^{3+})$ where $0.32 \leq m \leq 1$, $1.29 \leq y \leq 6\%$, $0.65 \leq z \leq 4\%$, $1.29 \leq h \leq 8\%$ in atomic ratio), were annealed in air at 1150°C for 4 h; (d) same as (c), but annealed at 1400°C in $40\% \text{H}_2/\text{He}$ for 4 h; (e) La (or $\text{GdF}_3\text{Sr}_n\text{AlO}_x\text{Eu}_y^{2+3+}$ where $0.178 \leq m \leq 0.714$, $0.17 \leq n \leq 0.4$, $0.75 \leq y \leq 16.7\%$ in atomic ratio), were annealed at 1150°C in $4\% \text{H}_2/\text{Ar}$ for 4 h. All substrates are $1\text{ in.} \times 1\text{ in.}$ and each site is $1\text{ mm} \times 2\text{ mm}$; thin films are $0.4\text{ }\mu\text{m} - 1\text{ }\mu\text{m}$ thick. Sputtering was carried out at $10^{-5} - 10^{-6}$ Torr base pressure, with Ar sputtering gas and a deposition rate of $0.1 - 0.5\text{ A/s}$. The images were taken with a UV lamp (UVP, UVGL-25 mineralight). The indicated sites correspond to the elemental compositions and stoichiometries of samples listed in Table I. Set 1 and Set 2 samples in library (a) are identical sample groups.

higher quantum efficiencies were obtained for samples with stoichiometries corresponding to the thin film library samples with brighter luminescence. The only exception is that efficient blue phosphors ($\text{QE} \sim 60\%$) were found only in thin film samples of $\text{LaAl}_3\text{O}_x\text{Eu}_0^{2+}$; bulk samples had considerably reduced quantum efficiencies (approximately 20%), probably due to the differing behavior of film and powder samples to processing under strongly reducing atmospheres.

Libraries also provide considerable information on the relationship between compositions and luminescence properties. In general, for the activators Eu^{3+} and Eu^{2+} , Y_mAlO_x hosts⁶ had reduced luminescence intensities relative to $\text{La}_m(\text{Sr}_n)\text{AlO}_x$ hosts, and $\text{La}_m(\text{Sr}_n)\text{AlO}_x$ hosts had reduced luminescence intensities relative to $\text{Gd}_m(\text{Sr}_n)\text{AlO}_x$ hosts. These results are consistent with the fact that the ionic radii of Gd^{3+} and La^{3+} are better matched to the rare earth activators than Y^{3+} ; and Gd^{3+} is more efficient in energy transfer to activators than La^{3+} .^{9,11} We also found that activators can be accommodated at high concentrations (up to 8%) without significant quenching of luminescence, suggesting that quenching by energy transfer between activators is inefficient in this host. Finally, the inclusion of fluoride ion in the

synthesis of $(\text{Gd}_{0.46}\text{Sr}_{0.31})\text{Al}_{1.23}\text{O}_x\text{F}_{1.38}\text{Eu}_{0.06}^{2+}$ increases the luminescence efficiency relative to the same starting composition lacking fluoride.

As expected, processing temperature and atmosphere also significantly affect luminescent properties. For example, powder samples of the composition $\text{Gd}_{0.46}\text{Sr}_{0.31})\text{Al}_{1.23}\text{O}_x\text{F}_{1.38}\text{Eu}_{0.06}^{2+}$ had a more intense green luminescence ($\text{QE} \geq 94\%$) when synthesized at 1375°C in $10\% \text{H}_2/\text{He}$ than at 1150°C in $10\% \text{H}_2/\text{He}$ ($\text{QE} = 42 \pm 5\%$); the composition $\text{GdAlO}_x\text{Eu}_{0.08}^{3+}$ had a more intense red luminescence ($\text{QE} = 85 \pm 5\%$) when annealed in air at 1400°C than at 1150°C ($\text{QE} = 40 \pm 5\%$). These results are consistent with our x-ray diffraction studies which indicate that the higher intensity luminescence is directly correlated with the formation of mostly a single phase perovskite structure. In the case of the $\text{La}_m\text{AlO}_x\text{Eu}_y^{2+}$ thin film blue phosphors, processing in a H_2 atmosphere at temperatures above 1300°C is also required, consistent with more complete reduction of the Eu activator. Even under these strongly reducing conditions, red phosphors were still obtained with strong luminescence and good chromaticity at the $\text{Gd}_m\text{AlO}_x\text{Eu}_y^{3+}$ thin film sites containing fluoride ion [Figs. 1(b) and 1(d)].

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(1) $\text{GdAlO}_x\text{Eu}^{2+3+}$
(2) $\text{Gd}_{0.77}\text{Al}_{1.22}$
(3) $\text{GdAlO}_x\text{Eu}^{3+}$
(4) $\text{Gd}_{0.69}\text{Al}_{1.43}$
(5) $\text{La}_{0.57}\text{Al}_{1.43}$
(6) $\text{La}_{0.5}\text{Al}_{1.5}\text{O}$
(7) $\text{La}_{0.43}\text{Sr}_{0.24}$
(8) $(\text{Gd}_{0.46}\text{Sr}_{0.31})\text{Al}_{1.23}\text{O}_x\text{F}_{1.38}\text{Eu}_{0.06}^{2+}$
(9) $\text{Gd}_{0.59}\text{Sr}_{0.18}$

Samples 1–8 elemental composition describes the nominal composition of an ideal perovskite phosphor Ce^{3+} (green, Ce^{3+} (Ref. 6). It was a 42% weight coefficient was used in automatic light at wavelength required to measure the H_2 , a 42% partial pressure was 16.7 psi, yielding large. In order to quantitative comparative quantum efficiency

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$\text{Gd}_{0.46}\text{Sr}_{0.31}$ ity ($x = 0.2$ vated gre y = 0.55) u phosphors mosphere broad green composition $\text{La}_{0.5}\text{Al}_{1.5}\text{O}$ and are exp peratures c range of 2 $^\circ\text{C}$ requireme tions (e.g., fraction an have the I (Relative structure.) compositio have a mi additional the optimu phase pho rable quan

TABLE I. Properties of optimized tricolor $\text{Gd}(\text{Sr},\text{La})\text{AlO}_x$ phosphors.

Sample nominal compositions	Synthesis conditions (°C), 4 h	Relative quantum efficiency (%)
(1) $\text{GdAlO}_x : \text{Eu}^{3+}$ (R)	1400 air	85
(2) $\text{Gd}_{0.77}\text{Al}_{1.23}\text{O}_x : \text{Eu}^{3+}$ (R)	1400 air	98
(3) $\text{GdAlO}_x : \text{Tb}_{0.08}$ (G)	1150 H_2/Ar	31
(4) $\text{Gd}_{0.69}\text{Al}_{1.31}\text{O}_x : \text{Ce}_{0.28}^{3+} : \text{Tb}_{0.041}^{3+}$ (G)	1375 H_2/He	37
(5) $\text{La}_{0.57}\text{Al}_{1.43}\text{O}_x : \text{Ce}_{0.23}^{3+} : \text{Tb}_{0.034}^{3+}$ (G)	1375 H_2/He	5
(6) $\text{La}_{0.5}\text{Al}_{1.5}\text{O}_x : \text{Eu}_{0.04}^{2+}$ (B) film	1375 H_2/He	60
(7) $\text{La}_{0.43}\text{Sr}_{0.24}\text{Al}_{1.33}\text{O}_x : \text{Eu}_{0.10}^{2+}$ (G)	1375 H_2/He	60
(8) $(\text{Gd}_{0.46}\text{Sr}_{0.31})\text{Al}_{1.23}\text{O}_x : \text{F}_{1.38} : \text{Eu}_{0.06}^{2+}$ (G)	1375 H_2/Ar	99
(9) $\text{Gd}_{0.59}\text{Sr}_{0.18}\text{Al}_{1.23}\text{O}_x : \text{Eu}_{0.06}^{2+}$ (G)	1375 H_2/Ar	90

Samples 1–8 (except No. 6) are bulk powder samples and correspond in elemental composition to the circled samples in Fig. 1. The notation describes the nominal composition and is not meant to indicate lattice sites or an ideal perovskite structure. Quantum efficiencies are relative to the commercial phosphors, $\text{Y}_2\text{O}_3 : \text{Eu}^{3+}$ (red, QE=97%) (Ref. 6), $\text{LaPO}_4 : \text{Tb}^{3+}, \text{Ce}^{3+}$ (green, QE=93%) (Ref. 6), and $\text{BaMgAl}_10\text{O}_{17} : \text{Eu}^{2+}$ (blue, QE=90%) (Ref. 6). It was determined that the differences in the absorption and reflection coefficients are small. Thick (>1 mm) compacted powder samples were used in the measurement. The samples were excited with monochromatic light at $\lambda_{\text{max}}^{\text{ex}}$, flux determined prior to incidence on samples and the wavelength response of the photomultiplier was corrected. The accuracy in the measurement of quantum efficiency is $\pm 5\%$. For processing under H_2 , a 42% partial pressure of H_2 in He or Ar was used and the total pressure was 16.7 psi; sintering was carried out at the indicated temperatures for 4 h, yielding largely single phase compounds as determined by x-ray diffraction. In order to quantify the luminescent efficiency of the thin film phosphors, comparative measurements were made with thin film phosphors of known quantum efficiencies.

Thus tricolor phosphors can be synthesized with the same activator (Eu) in a perovskite host under reducing conditions [Fig. 1(b)]. Again, these results underscore the importance of including processing conditions as a parameter in the combinatorial search.

The phosphor with the composition $\text{Gd}_{0.46}\text{Sr}_{0.31}\text{Al}_{1.23}\text{O}_x : \text{F}_{1.38} : \text{Eu}_{0.06}^{2+}$ (green) has better chromaticity ($x=0.27, y=0.58$) than that of the standard Tb^{3+} activated green phosphor $\text{Y}_3(\text{Al},\text{Ga})_5\text{O}_{12} : \text{Tb}$ ($x=0.36, y=0.55$) used in projection TVs. The chromaticity of these phosphors can be tuned by changing either the reducing atmosphere during processing or the Sr concentration. The broad green and blue luminescence in phosphors with the compositions $\text{Gd}_{0.46}\text{Sr}_{0.31}\text{Al}_{1.23}\text{O}_x : \text{F}_{1.38} : \text{Eu}_{0.06}^{2+}$ and $\text{La}_{0.5}\text{Al}_{1.5}\text{O}_x : \text{Eu}_{0.04}^{2+}$ are characteristic of $5d$ to $4f$ transitions and are expected to have short lifetimes. The quenching temperatures of all the phosphors listed in Table I are in the range of 250–350 °C and they are chemically stable in air, a requirement for applications under harsh excitation conditions (e.g., plasma displays and projection TVs). X-ray diffraction analysis of selected powder samples shows that all have the perovskite structure, with significant defects.^{12,13} (Relative peak intensities differ significantly from the ideal structure.) The powder sample of the green phosphor, with composition $\text{Gd}_{0.46}\text{Sr}_{0.31}\text{Al}_{1.23}\text{O}_x : \text{F}_{1.38} : \text{Eu}_{0.06}^{2+}$ was found to have a minority phase ($\sim 5\%$) of SrAl_2O_4 . The synthesis of additional powder samples with stoichiometries near that of the optimal phosphor in the library afforded a near single phase phosphor, $\text{Gd}_{0.59}\text{Sr}_{0.18}\text{Al}_{1.23}\text{O}_x : \text{Eu}_{0.06}^{2+}$, with a comparable quantum efficiency ($QE=90\pm 5\%$).

ons: (a) La or h; (b) same as $\varepsilon_z \leq 4\%$, 1.29 h; (c) La (or Ar for 4 h. All pressure, with ε_z correspond to ups.

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Sun et al.

Appl. Phys. Lett., Vol. 70, No. 25, 23 June 1997

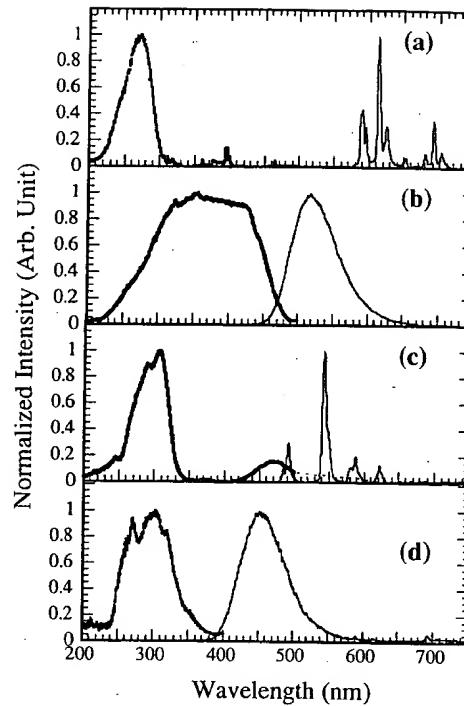


FIG. 2. (a) Photoluminescent spectra of (a) $\text{Gd}_{0.77}\text{Al}_{1.23}\text{O}_x : \text{Eu}^{3+}$ (sample 2, Table I); (b) $\text{Gd}_{0.46}\text{Sr}_{0.31}\text{Al}_{1.23}\text{O}_x : \text{F}_{1.38} : \text{Eu}_{0.06}^{2+}$ (sample 8, Table I); (c) $\text{Gd}_{0.69}\text{Al}_{1.31}\text{O}_x : \text{Ce}_{0.028}^{3+} : \text{Tb}_{0.04}^{3+}$ (sample 4, Table I); and (d) (Relative peak intensities) (sample 6, Table I) powder phosphors. Spectra were measured with F-4500 Hitachi spectrophotometer, exciting at the maximum absorption of each compound.

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